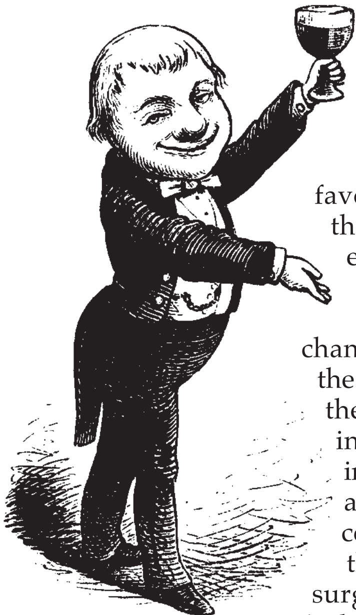
Investigation and Remediation

With the Possible Phase Out of MTBE, What Do We Know About Ethanol?

by Bruce Bauman



Let's toast the fortunes of humankind's favorite beverage, that inebriating elixir—ethanol. There is a reasonably good chance that within the next five years, the use of ethanol in gasoline could increase as much as 200 to 300 percent! With luck, that potential surge in demand won't drive up the cost of your Saturday night Wild Turkey.

A quick recap will help explain this possible boost to domestic fuel ethanol utilization, and then on to the UST/groundwater implications. MTBE and ethanol are the two most widely used oxygenates—according to the Department of Energy, in 1997 about five times as much MTBE as ethanol was used in gasoline in the United States. Other oxygenates (TAME, ETBE, DIPE, methanol, TBA) are used in only a very small percentage of gasoline.

Oxygenates are blended into conventional gasoline to provide economical octane, typically at low volumes (e.g., less than 1–5 vol %); higher volumes are found in premium gasolines than in "regular." Many urban areas of the United States are required to use reformulated gasoline (RFG) to reduce emissions that contribute to ozone formation. As required by Congress in the 1990 Clean Air Act (CAA) amendments, RFG must contain at least 2 percent oxygen by weight (about 11% volume MTBE or 6% ethanol).

In a much smaller number of urban areas, "oxyfuel" must be used in winter months to reduce carbon monoxide emissions. Oxyfuel must contain at least 2.7 percent oxygen by weight (about 15 % volume MTBE or 8% ethanol). EPA's Office of Air maintains an excellent Web site that can give you details on which parts of the United States must use these special gasolines *(http://www.epa.gov/oms/ fuels.htm)*. (NOTE: Ethanol is sometimes used at 10 percent volume in gasoline, because there is a 5.4 cent/gallon federal subsidy. Smaller subsidies apply to gasoline using less ethanol.)

You are probably familiar with California's decision to phase out the use of MTBE in gasoline by December 2002. Currently, about 70 percent of the gasoline sold in California is RFG. (California has some specific regulatory gasoline requirements that make its RFG different than that found in the rest of the country, but it still needs to contain 2% oxygen by weight.) When MTBE is completely phased out, ethanol is the logical replacement oxygenate (assuming the CAA "oxygen mandate" is not repealed). This is no trivial issue from the supply perspective. Given that California uses so much gasoline and currently uses very little ethanol, this ethanol-for-MTBE substitution would require almost 50 percent of the current U.S. ethanol production capacity!

A tank that is closed and left in place is still an environmental threat if it has not been properly closed and a headache for state UST/LUST program personnel, who will have to see that owners and operators finish the job or, in many cases, hope that someone steps forward to claim responsibility for the tank.

Ethanol in Groundwater?

All of this information is just background to get around to the main question: What do we know about the behavior of ethanol in groundwater? Many of you who are reading this article have been responsible for overseeing UST sites where ethanol was released—especially in parts of the Midwest, where ethanol has found its greatest marketability. States like Nebraska have strongly supported and subsidized ethanol production to enhance both their economies and promote "energy security" (i.e., every barrel of ethanol produced for use in gasoline means one less barrel of oil that needs to be imported). In Illinois, an ethanol-in-diesel ("biodiesel") demonstration program is in progress.

For almost a decade, however, I have attempted at infrequent intervals to unearth real-world field information on ethanol or ethanol–gasoline releases, but I have not been able to find much. I began my search in the late 1980s, when the American Petroleum Institute (API) was conducting the only known field study on alcohol fate and transport in groundwater.

We looked at methanol, as it was being seriously evaluated by California as a cleaner-burning gasoline substitute. We injected three simulated dissolved plumes side by side in the world-famous Borden Aquifer in Canada: (1) a typical BTEX plume, (2) a BTEX and MTBE plume, and (3) a methanol and BTEX plume. The plumes were monitored intensively for about 16 months, and mass balances were performed at the end of the experiment.

To briefly summarize the University of Waterloo report, the methanol did biodegrade to below detection limits (250 ppb), but the BTEX in that plume biodegraded much less than in the "BTEX only" plume, or the MTBE-BTEX plume.

Unless someone can provide evidence to the contrary, I would expect that the subsurface fate/behavior of methanol and ethanol would be fairly similar. So what does this simi-

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larity mean for real-world ethanol-gasoline releases? It suggests that at least for some release scenarios, ethanol-BTEX plumes would likely be a bit longer than "typical" BTEX plumes.

From a practical perspective, this potential plume elongation may not be very relevant for most RBCA evaluations, especially if it's only 1 to 200 feet or so. However, it would seem prudent for at least some situations, especially in Midwestern states where ethanol is the dominant oxygenate, to determine if ethanol is present at the release site and assess what its effects might be on the benzene plume.

Biodegradability and Other Knowledge Gaps

Despite this ethanol field data "black hole," several recent assessments of potential groundwater impacts from such UST releases seem to rather blithely assume that there will be no impacts, because ethanol is considered to be so biodegradable. For example, the comprehensive University of California evaluation of MTBE that formed the basis for that state's recent decision to phase out MTBE states that "Ethanol plumes will biodegrade fairly rapidly." The study does raise the issue of "preferred substrate utilization" and its potential impacts on the length of BTEX plumes (i.e., as the microbial population will prefer to extract its energy from the available ethanol, the onset of significant biodegradation of BTEX could be delayed by several days, weeks, months, depending on numerous site/release-specific factors).

The operative phrase here is "biodegrade fairly rapidly." How rapid is rapid? Furthermore, as no field data exist on this topic , these assessments are simply taking laboratory biodegradation data and extrapolating them to field situations. Most of us would agree that one must use a great deal of caution in making that lab-to-field leap.

Finally, it is very important to consider different release scenarios and their implications for ethanol-BTEX dissolved plume development. Most folks would agree that for small, slow, continuous releases (e.g., 2-10 gal/day), dissolved ethanol would be rapidly biodegraded. However, if there is a large sudden release (e.g., 500-plus gallons in one day), the mass of ethanol that might be dissolved would be very large, and it might take a very long time (months?) for it degrade.

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number of other issues regarding ethanol-gasoline releases to groundwater that need to be thought through before we begin a massive migration to dependence on ethanol for all of our gasoline oxygen needs:

■ **Maximum dissolved ethanol concentrations** Because ethanol is miscible with water (completely soluble), very high concentrations are likely to occur near the source of the release, perhaps as high as 10,000 ppm or more. Although ethanol may be rapidly biodegraded, at these concentrations it will be toxic to microorganisms. Biodegradation will occur, of course, at the diluted fringes of the ethanol plume, but this much dissolved mass will take a long time to biodegrade, even at very high substrate utilization rates.

■ **Plume elongation caused by electron acceptor depletion** If the rapid biodegradation of ethanol uses up all of the available electron acceptors needed for aerobic and anaerobic biodegradation (e.g., oxygen, iron, sulfate), will BTEX biodegradation be impeded?

■ **Cosolubility of BTEX** Several authors have looked at the potential for methanol or ethanol to increase the dissolved-phase concentration of BTEX. In general, the lab results seem to suggest that at the 5 to 10 percent volume concentrations found in gasoline, ethanol would not enhance the solubility of BTEX significantly. However, for releases of neat (pure) ethanol (see below), cosolubility effects would greatly increase dissolved BTEX.

■ **Trace compounds in fuel-grade ethanol** The presence of TBA in fuel-grade MTBE has been identified as an issue for MTBE release sites. Are there trace compounds in fuel-grade ethanol that might be of concern and that would be less biodegradable than ethanol?

■ **Neat ethanol releases** Unlike MTBE, which is blended at the refinery and then shipped through pipelines or tankers/barges, ethanol must be blended at the distribution terminal just prior to delivery to the end user. This requirement arises because the presence of as little as 1 percent water can cause "phase separation" of an ethanol-gasoline mixture into an alcohol-rich phase and a hydrocarbon-rich phase. Thus pure ethanol must be stored at terminals in separate tankage, which could also have a release and require remediation at some time.

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What Information Is or Is Not Yet Out There?

If you're looking for a good summary of what we know and don't know about ethanol in groundwater, get a copy of *Evaluation of the Fate and Transport of Ethanol in the Environment*, a report from the American Methanol Institute by Malcom-Pirnie (keep in mind that methanol is a primary feedstock for making MTBE). It is the single best source of information available today.

Information on ethanol's health effects and a much briefer environmental summary are accessible from the Renewable Fuels Association, at *http://www.ethanolrfa.org/544_er_1999.html* (keep in mind that RFA is an ethanol advocacy organization).

API is just beginning its own ethanol literature review and some laboratory studies evaluating whether the "preferred substrate" hypothesis is legitimate. It hopes to have this complete within the next four to six months.

Also of interest is some work going in Brazil, where gasoline with 20 to 25 percent ethanol has long been in use as a motor fuel. A field-release experiment on this kind of gasoline was just started by Brazilian researchers late last year, and initial results should be forthcoming within another year or so.

Finally, as required in the MTBE phase-out Executive Order Governor Davis signed in March, CalEPA needs to issue a report on ethanol environmental impacts by the end of this year. As this time, it is considering contracting for $650,000 in ethanol fate and transport studies in surface and groundwater, trying to quickly come up to speed. Ideally, the agency's work will also shed some much-needed light on this issue.

The Jury's Still Out

So will we actually see this large increase in ethanol use in gasoline over the next several years? It is difficult to say, as there are more than a few tricky variables in this equation. It is likely that MTBE use will decline, and if the federal oxygen mandate is not changed, increased ethanol use is inevitable. However, Congress may amend the CAA to specifically address this MTBE-ethanol issue through repeal of the oxygen mandate. There is increasing evidence that lots of oxygen is not really needed in our gasoline.

Several mandate repeal bills are under discussion in the Senate and House, and others are being discussed for potential consideration. Some of the bills would specifically target California, as it has already acted to phase out MTBE and is facing an ethanol mandate. (For an interesting review of some of this activity, see the testimony of a variety of people at the May 6 House of Representatives Committee on Commerce hearing on HR 11, one of California-specific bills, at *http://com-notes.house.gov/cchear/hearings106.nsf/hemain.*)

Other bills would remove the mandate for the entire country. Congress is very aware of the activities of the EPA Oxygenate Blue Ribbon Panel, which appears to be leaning toward recommending a removal of the mandate, and also the National Research Council's recent report that downplayed the benefits of oxygenate use for ozone reduction. But if you think that science and facts will win the day with the political poohbahs in the Capitol, maybe you've had a little too much to drink. ■

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